

# U. S. Army Communications- Electronics Command

## Night Vision & Electronic Sensors Directorate

**Title:** Study and Development of Polymeric  
Photorefractive Materials

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**Type of Report (Final, Interim, etc.):**

Final

**Date:** November 21, 1995

### Contract Number

DAAB07-91-C-K767

### Report Number

NV-96-C02

DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution Unlimited



Fort Belvoir, Virginia 22060-5806

19960221 061

DTIC QUALITY ASSURED 1

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release Distribution Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A			5. MONITORING ORGANIZATION REPORT NUMBER(S) NV-96-C02		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			7a. NAME OF MONITORING ORGANIZATION U.S. Army CECOM NVESD		
6a. NAME OF PERFORMING ORGANIZATION IBM Corporation Almaden Research Center		6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) 10221 Burbeck Road, Suite 430 Ft. Belvoir, VA 22060-5806		
6c. ADDRESS (City, State, and ZIP Code) 650 Harry Road San Jose, CA 95120-6099		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAB07-91-C-K767			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ARPA		8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS		
8c. ADDRESS (City, State, and ZIP Code) 3701 N. Fairfax Drive Arlington, VA 22203-1714		PROGRAM ELEMENT NO. 62301E	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Study and Development of Polymeric Photorefractive Materials					
12. PERSONAL AUTHOR(S) Dr. Donald M. Burlland					
13a. TYPE OF REPORT FINAL		13b. TIME COVERED FROM 9/30/91 TO 9/30/95		14. DATE OF REPORT (Year, Month, Day) 95 11 21	
15. PAGE COUNT 31					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
20	05				
20	06				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The research program summarized here involved the development of new organic photorefractive polymers, improvements of our understanding of the fundamental phenomena that govern photorefractivity in these polymer systems and an optimization of the material's properties for practical device applications. Of particular emphasis were systems that might be of use as optical limiters in eye and sensor protection devices. At the time that the work supported under this Contract began, photorefractive polymers had just been discovered at IBM's Almaden Research Center. The first polymer system discovered was slow and its steady state diffraction efficiency was small. It was no match for the inorganic crystalline photorefractive materials that had been under investigation for over 20 years at that time. Substantial progress has been made and as a result of this ARPA (ARMY) supported work, photorefractive polymers are now equal in speed and efficiency to some of the best inorganic crystalline systems. Improvements continue to be made both by our group at IBM and by others and there is reason to expect that in the near future the polymeric systems will surpass the inorganic crystals in their photorefractive polymers.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION U		
22a. NAME OF RESPONSIBLE INDIVIDUAL Byong H. Ahn			22b. TELEPHONE (Include Area Code) (703) 704-2031		22c. OFFICE SYMBOL AMSEL-RD-NV-ST-AL

# **FINAL TECHNICAL REPORT**

## **Study and Development of Polymeric Photorefractive Materials**

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Research Division  
Almaden Research Center  
650 Harry Road  
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Principal Investigator: Donald M. Burland

November 21, 1995

## EXECUTIVE SUMMARY/CONCLUSIONS

The research program summarized here involved the development of new organic photorefractive polymers, improvements of our understanding of the fundamental phenomena that govern photorefractivity in these polymer systems and an optimization of the materials properties for practical device applications. Of particular emphasis were systems that might be of use as optical limiters in eye and sensor protection devices. At the time that the work supported under this contract began, photorefractive polymers had just been discovered at IBM's Almaden Research Center. The first polymer system discovered was slow and its steady state diffraction efficiency was small. It was no match for the inorganic crystalline photorefractive materials that had been under investigation for over 20 years at that time. Substantial progress has been made and as a result of this Army (ARPA) supported work photorefractive polymers are now equal in speed and efficiency to some of the best inorganic crystalline systems. Improvements continue to be made both by our group at IBM and by others and there is reason to expect that in the near future the polymeric systems will surpass the inorganic crystals in their photorefractive polymers.

The significant accomplishments achieved as part of the Army (ARPA) supported work described in this Final Report are summarized below:

- ♦ A wide range of photorefractive polymers have been investigated. The steady state diffraction efficiency and the grating growth rate have both been improved by more than four orders of magnitude. This factor of  $10^8$  improvement in overall performance is impressive, particularly when one notes that no limits to future improvements have yet been encountered.
- ♦ Two beam coupling gain, necessary for beam fanning, has been observed for the first time in several polymeric systems. Beam fanning is the critical property utilized in eye and sensor protection devices.

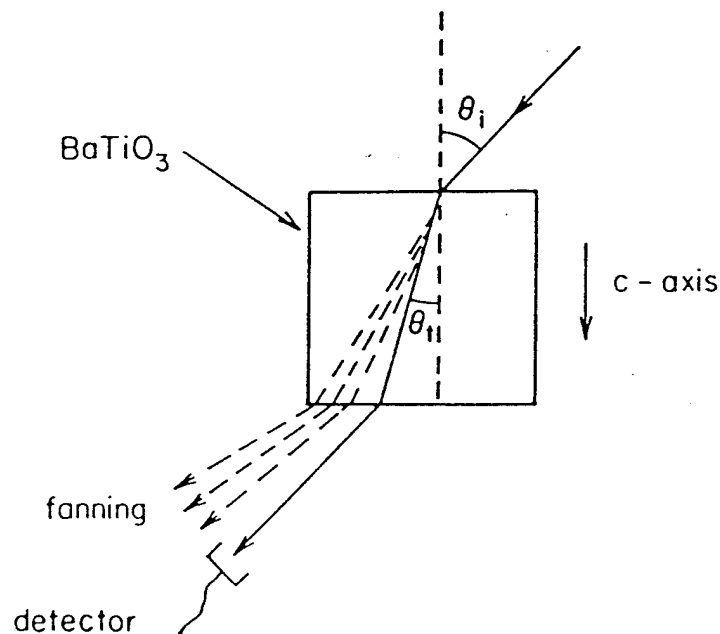
- ♦ A new photorefractive mechanism has been identified that can only occur in polymer systems. This orientational enhancement mechanism can result in an order of magnitude or more improvement in the steady state efficiency of a photorefractive grating.
- ♦ Investigations of limitations on the sensitivity of photorefractive polymers indicate that the quantum yield for charge carrier generation is the primary limiting factor at present. This finding points the way to approaches for improving the photorefractive properties of polymer systems.
- ♦ An approach to the production of thick samples, stratified volume holographic optical elements (SVHOE), has been adapted for and demonstrated in photorefractive polymers. Thick samples will be necessary for the utilization of these polymers in applications where beam fanning is important. SVHOE's provide one way of producing these thick samples.

## **I. Contract Goals**

In the original contract proposal submitted by IBM to the Army (ARPA), IBM proposed to identify and study polymeric materials that exhibit the photorefractive (PR) effect and to understand the underlying microscopic nature of the effect using laser spectroscopic techniques.

At that time W.E. Moerner and his colleagues at IBM's Almaden Research Center had just identified the first PR polymer system. This discovery opened up the possibility of a new class of PR materials with improved properties for applications such as holographic optical data storage and beam fanning for power limiting. These PR polymers possessed a number of significant fabrication advantages over crystalline materials such as low temperature processing, compatibility with a variety of substrate materials including integrated electronic and optoelectronic components, bulk forming by injection molding or extrusion, thin film fabrication by spin-coating or plasma deposition and device patterning by etching or photochemical processing.

Of particular emphasis in the work proposed would be the application of the photorefractive effect for optical limiting using the phenomenon of PR beam fanning. Optical limiting is important for eye and sensor protection. Figure 1 illustrates the concept of beam fanning. Light from a laser is incident on a photorefractive material with high gain. Nearly all of the laser power is scattered asymmetrically into a broad fan of light resulting from amplification of scattered radiation by two-beam coupling. Advantages of this approach to optical limiting include deflection, rather than absorption of the optical power, response to low light intensities, and a simple refresh cycle.



**Figure 1.** Schematic representation of optical limiting by beam fanning in a photorefractive material.

Specifically IBM proposed investigations of PR polymers focused in three areas:

- ♦ Development of new organic PR polymers
- ♦ Understanding of PR in polymers
- ♦ Optimization of PR polymer performance for eye and sensor protection applications.

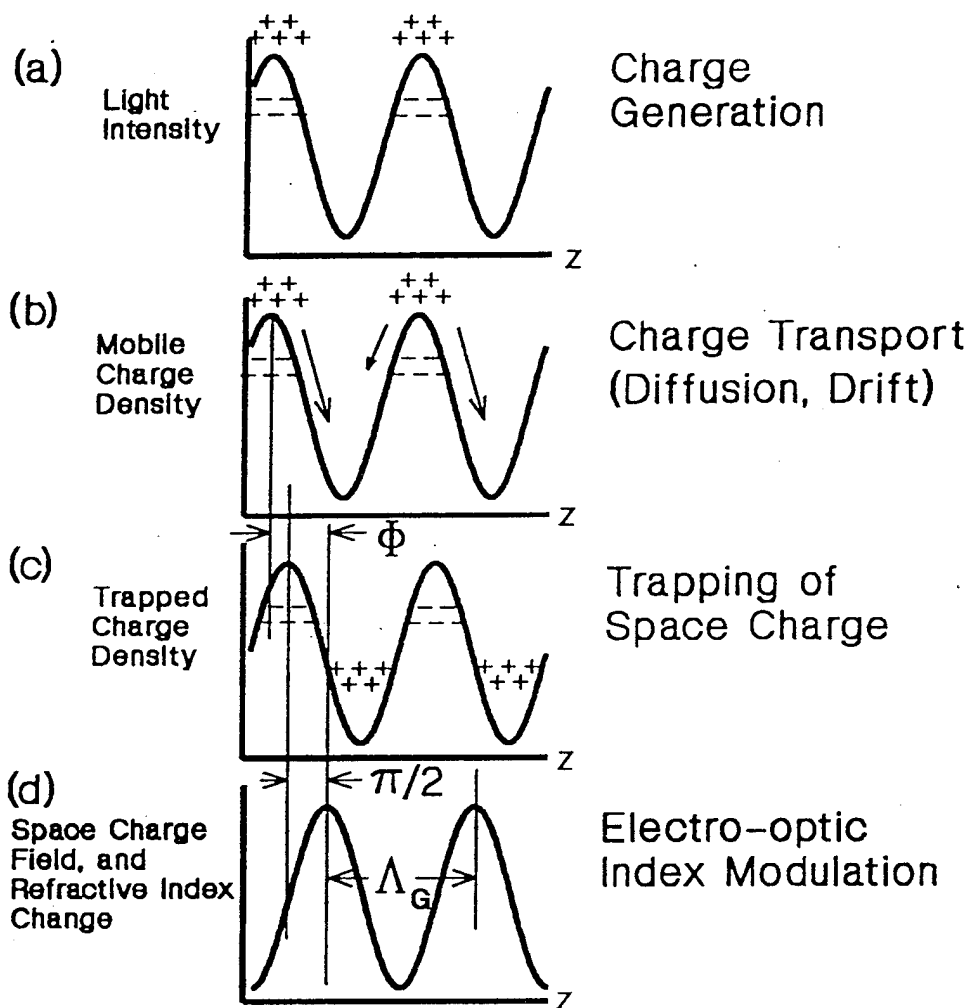
Each of these three areas will be discussed separately in the remainder of this report, after a brief introduction on the fundamentals of the PR effect. More detail can be found in the publications related to this Army (ARPA) supported work found in the Appendix.

## II. Fundamentals of the Photorefractive Effect in Polymers

The PR effect can occur in certain materials which are photoconductive and show a dependence of the optical index of refraction upon electric field. The ingredients necessary for producing a PR-material are therefore: a photoionizable charge generator, a transporting medium, trapping sites, and a dependence of the index of refraction upon space-charge field. However, the simple presence of these elements in a material does not guarantee that an experimentally observed diffraction grating produced by optical illumination necessarily arises from the photorefractive effect.

Figure 2 shows the process of PR grating formation. Figure 2a shows the optical standing wave pattern of intensity that is produced by two intersecting coherent beams of light. This time-independent but spatially modulated intensity pattern consists of light and dark planes across the PR material. The first physical process required for the PR effect is the generation of mobile charge in response to the spatially varying illumination. This may be viewed as the separation of electrons and holes indicated as plus and minus charges in the Figure. In organic materials, this effect is strongly electric field dependent. The second element for the PR effect is transport of the generated charges, with one carrier being more mobile than the other. In Figure 1b, the holes are shown as being more mobile, which is by far the most common case for organics. The physical processes giving rise to charge transport are either diffusion due to density gradients, or drift in an externally applied electric field. Since most polymeric materials with sufficient optical transparency are relatively good insulators, the ability of generated charges to move by diffusion alone is quite limited and can, in most cases be neglected. The third element for the PR effect is the presence of trapping sites which hold the mobile charges. In most PR materials, the exact identity of the trapping sites is not known in detail.





**Figure 2.** Illustration of photorefractive grating formation : (a) charge generation occurs at light intensity maxima; (b) mobile photogenerated charges migrate by diffusion or drift in the presence of an external electric field; (c) the charges trap at the light intensity minima, which (d) creates a space charge field leading to a refractive index grating in materials which are electrooptically active.

After separation of charge carriers occurs, the resulting space-charge density is shown in Figure 2c. Via Poisson's equation of electrostatics, such a charge distribution produces a sinusoidal space charge electric field shown in Figure 2d. Since Poisson's equation relates the

spatial gradient of the electric field to the charge distribution, the resulting internal electric field is shifted in space by 90° relative to the trapped charge.

Finally, if the optical index of refraction of the material changes in response to an electric field, a spatial modulation of the index of refraction results as shown in Figure 2d. For example, if the material has a linear electrooptic effect, the magnitude of the index modulation  $\Delta n$  is related to the magnitude of the space-charge field  $E_{sc}$  by the relation

$$\Delta n = -(1/2)n^3 r_e E_{sc} \quad (1)$$

where  $r_e$  is the effective electrooptic coefficient for the geometry under consideration. A sinusoidally varying index modulation is a grating which can diffract light. This index grating is shifted by 90° from the illumination pattern. It is this 90° phase shift that gives rise to phenomena such as beam fanning that is to be exploited in eye and sensor protection. The PR effect, as defined here, is distinct from the many other possible mechanisms of grating formation in optical materials, such as photochromism, thermochromism, thermorefraction, generation of excited states, etc.

Several physical effects are operative in organic materials which are not present in inorganic crystals. First, the quantum efficiency of charge generation  $\phi$  is expected to be highly electric field dependent. Absorption of a photon creates a bound electron-hole pair (a Frenkel exciton) and separation of this pair to create a free hole competes with geminate recombination, resulting in an electric field dependence for  $\phi$ . This is widely observed in organic photoconductors and is in contrast to the behavior observed in inorganic photorefractives, where  $\phi$  is independent of field.

Second, in inorganic photorefractive crystals, the mobility is, to a good approximation, independent of the electric field. In molecularly doped organic polymers, however, the mobility of the photogenerated charges is field (and temperature) dependent, with the mobility increasing as  $\ln(E)^{1/2}$  in many cases. We have verified this behavior in several PR polymers.

Third, the second-order nonlinearity must be induced in the polymer by applying an electric field to align the chromophores and remove the center of symmetry which would be present in a random distribution. The alignment of the molecules can be either permanent, in which case the molecules remain aligned after the field is removed, or temporary, in which case the molecules remain aligned only as long as the field is applied to the material. The scheme used most often for achieving stable poling is to heat the material to a temperature near the glass transition temperature  $T_g$ , apply an electric field to the material, cool the material to a temperature well below  $T_g$ , and then remove the field. At this lower temperature, the molecules are unable to easily relax back to a random distribution of orientations. However, if the  $T_g$  of the materials is sufficiently low such that the nonlinear optical (NLO) chromophores can be oriented at room temperature, the value of  $r_e$  is a function of the applied field and is generally observed to be linearly proportional to the field since saturation of the orientation is seldom achieved. This is the situation with many of the PR polymers that we and others have studied so far, and, due to a novel enhancement effect discovered as part of the work reported here and discussed below, the ability of the NLO chromophores to orient at ambient temperatures is actually an advantage.

### III. Development of New Photorefractive Polymers

The first photorefractive polymer, identified at the Almaden Research Center before the start of the ARPA supported work described here, consisted of the electrooptic(EO) polymer bisphenol-A-diglycidylether 4-nitro-1,2-phenylenediamine (BisA-NPDA) made photoconductive by doping with the hole transport agent diethylamino-benzaldehyde diphenylhydrazone (DEH). Based on this success, a variety of EO active polymers were synthesized and their PR properties measured in combination with a wide range of charge transport agents. The NLO polymers used are shown in Figure 3 and the charge transport agents in Figure 4. Also shown in Figure 4 are the

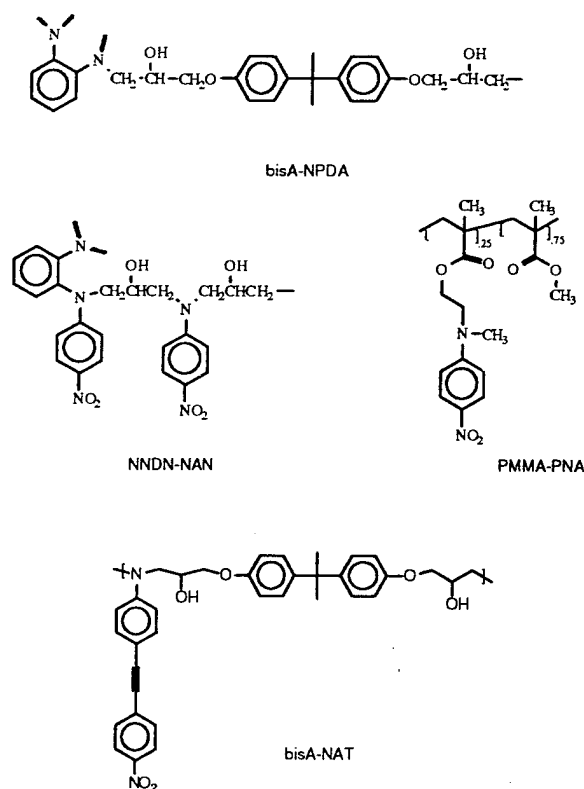
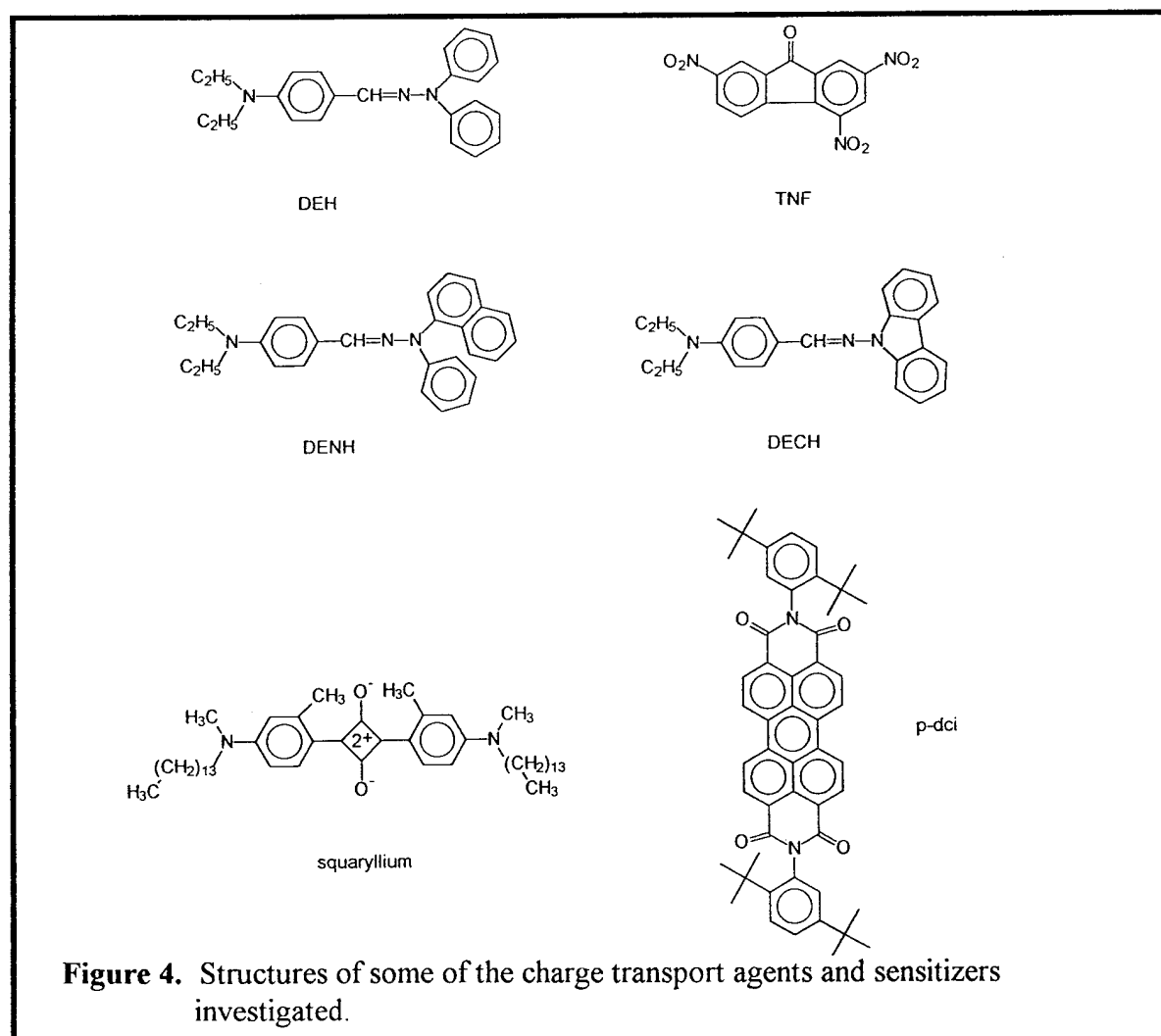


Figure 3. Structures of electrooptic polymers investigated.

sensitizers used to shift the PR polymer systems absorption into a convenient wavelength region for the lasers used. The results of these measurements are summarized in Table 1. In the Table  $\lambda$  is the wavelength used for writing and reading in a four wave mixing configuration,  $\alpha$  is the absorption coefficient,  $\eta_{ss}$  the steady state diffraction efficiency,  $\tau$  the grating growth time and  $\Gamma$  the two beam coupling coefficient. From the Table it can be seen that in all cases the steady state efficiency was low ( $<10^{-2}$ ), the growth rate at writing powers in excess of  $1\text{W}/\text{cm}^2$  was slow and no net two beam coupling gain was observed, i.e.  $\Gamma < \alpha$ . Two beam coupling gain is necessary to observe beam fanning.

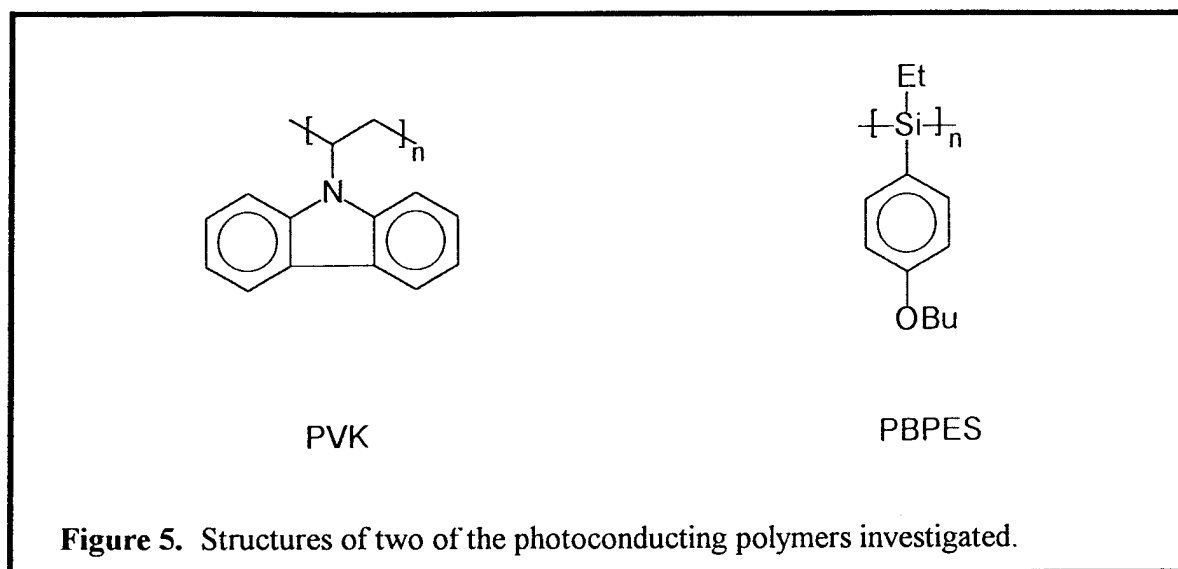


**Figure 4.** Structures of some of the charge transport agents and sensitizers investigated.

**Table 1. Optical Properties of Doped Materials Based on NLO Polymer Hosts**

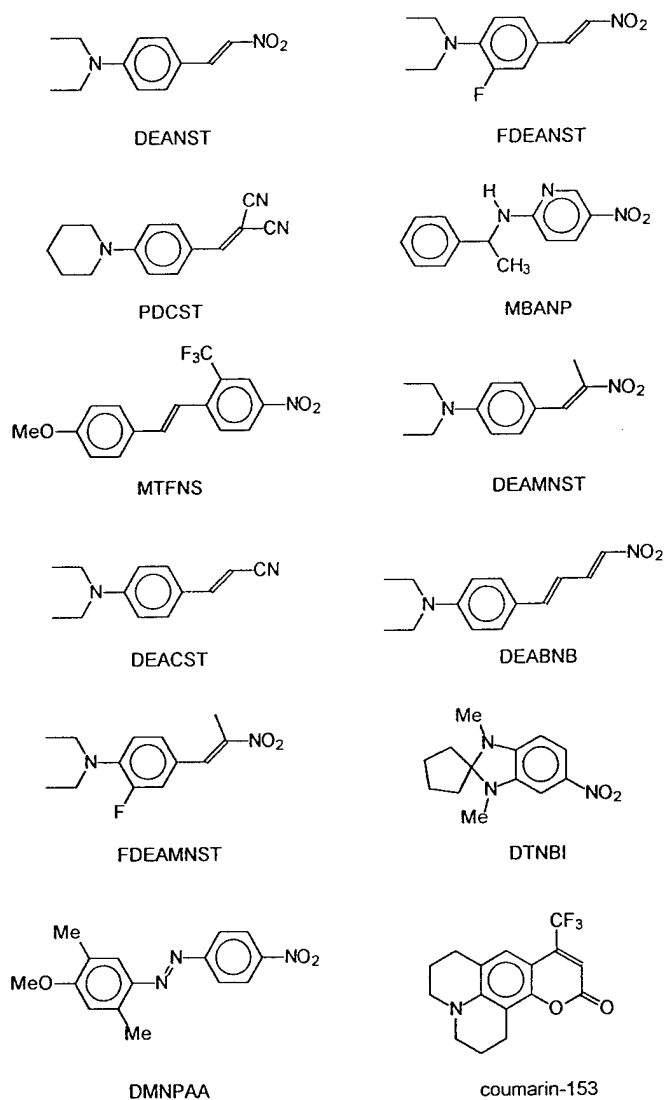
NLO polymer	CT agent	sensitizer	$\lambda$ (nm)	$\alpha$ (cm <sup>-1</sup> )	$\eta_{ss}$	$\tau$ (s)	$\Gamma$ (cm <sup>-1</sup> )
bisA-NPDA	DEH	none	647	10	$5 \times 10^{-5}$	100	0.33
bisA-NPDA	DENH	none	647	10	$1 \times 10^{-5}$		
bisA-NPDA	DECH	none	647	10	$9 \times 10^{-6}$		
NNDN-NAN	DEH	none	647		$1 \times 10^{-3}$		
PMMA-PNA	DEH	none	568	5.9	$1 \times 10^{-5}$	2	0.23
			647	1.1	$4.9 \times 10^{-6}$	7	0.11
PMMA-PNA	DEH	C <sub>60</sub>	647	3.4	$4.8 \times 10^{-5}$	0.25	0.6
PMMA-PNA	DEH	TNF	647	3.2	$1.1 \times 10^{-5}$	10	
PMMA-PNA	DEH	squaryllium	647	12	$1.8 \times 10^{-5}$	28	
PMMA-PNA	DEH	p-dci	647	2	$6.7 \times 10^{-5}$	9	
bisA-NAT	DEH	none	676	18			1.8
			753	2.4			1.2
bisA-NAT	DEH	none	650	118	$1.1 \times 10^{-2}$		

In order to improve on the steady state efficiency and the grating growth time, a class of polymers was next investigated in which the polymer itself was charge transporting and the system was made optically nonlinear by doping with an NLO active chromophore. Two polymers in this class



were investigated. The first and most thoroughly investigated of these polymers is poly(N-vinylcarbazole) (PVK) and the second is a poly(silane) derivative (see Figure 5).

Figure 6 shows some of the nonlinear chromophores that we have incorporated into charge transporting polymers. Of particular interest is the system PVK:FDEANST:TNF. This system was the first in which two beam coupling gain was observed. Two beam coupling gain is necessary for the beam fanning effect utilized in optical limiting devices. The chromophore FDEANST has reduced absorption in the red relative to the unfluorinated analog DEANST and therefore should eliminate absorption by the chromophore in the red and infrared region of the spectrum where the well-known PVK:TNF charge transfer complex absorbs. The PVK:TNF complex is here used as a sensitizer. The glass transition temperature of the 125 $\mu$ m thick films was approximately 40°C. Therefore these films could be poled at room temperature by the application of an electric field, and depoling occurred automatically when the E field was removed.



**Figure 6.** Structures of some of the nonlinear chromophores incorporated as guests in the photoconducting polymer hosts.

The photorefractive performance of PVK:FDEANST:TNF was significantly better than that of previously described organic photorefractive materials for several reasons.

PVK:FDEANST:TNF is the first organic material showing an internal two beam coupling gain coefficient  $\Gamma$  that exceeds the absorption coefficient. Its maximum diffraction efficiency of 1% is

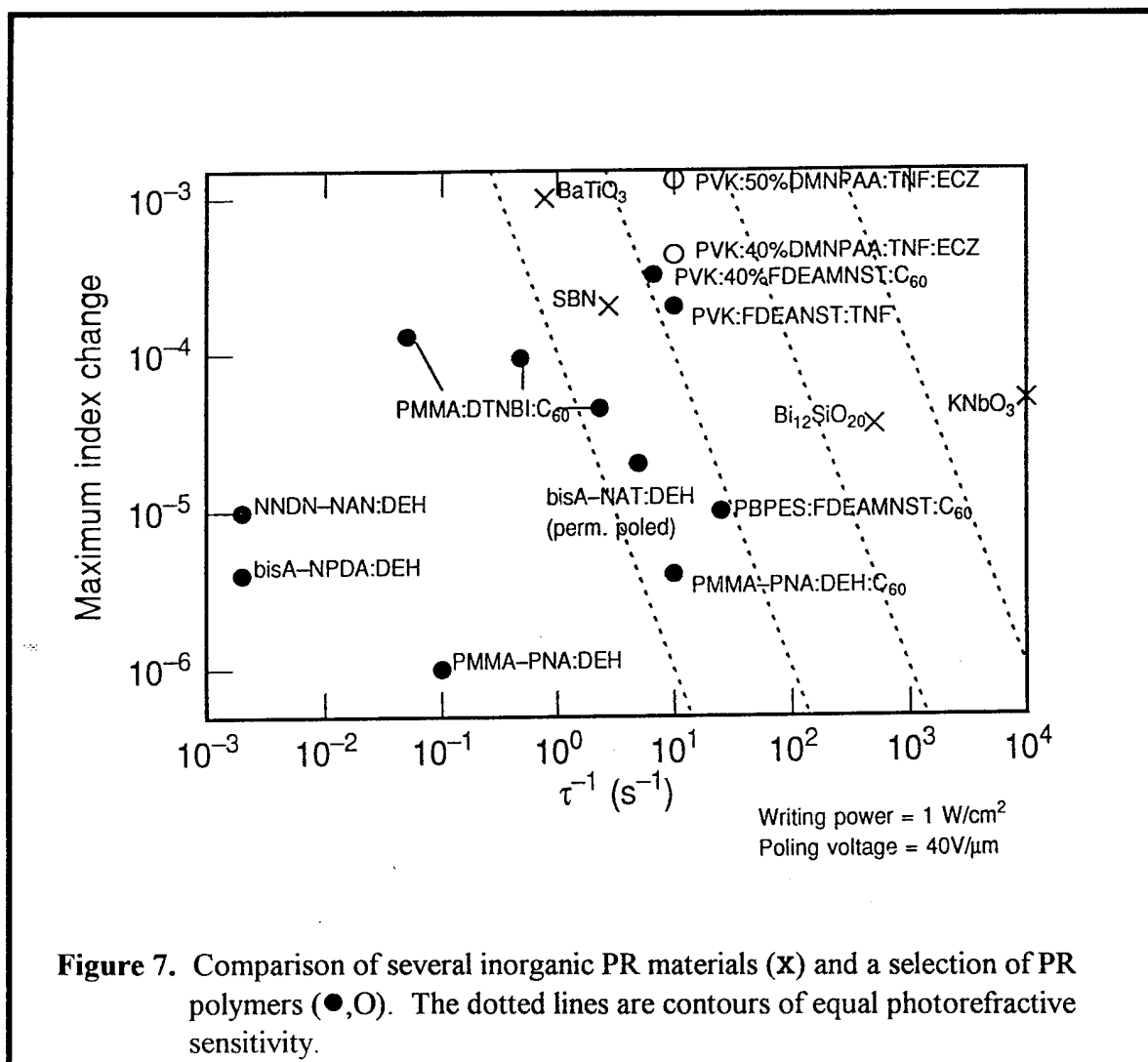


1-2 orders of magnitude larger than values previously reported for PR polymers. The grating growth time of about 100ms is comparable to that of the fastest known photorefractive polymer.

The generality of the photorefractive properties of PVK doped systems have been investigated by constructing other PVK-based polymers by varying both the chromophore and sensitizer. Some of the NLO chromophores used are shown in Figure 6 and the sensitizers in Figure 4. Results of measurements on these systems are shown in Table I. The utility of different sensitizers is reflected in the growth time  $\tau$ , which has the smallest value (fastest grating growth) for the sample containing the fullerene  $C_{60}$ . It is apparent that varying the sensitizer also influences both  $\eta_{ss}$  and  $\Gamma$ .  $C_{60}$  provides the largest PR response of the sensitizers studied. It is likely that in addition to providing increased generation of charges,  $C_{60}$  acts to increase the density of traps in the material.

The polymer system PMMA:DTNBI: $C_{60}$  represents another class of PR polymeric materials of particular interest. These class of materials have been called dual function dopant (DFD)-based PR polymers, in which a single small molecule species (DTNBI in this case) has the dual function of imparting both charge transport and NLO activity to the material while the polymer host functions only as an inert binder. A small amount of charge-generating sensitizer ( $C_{60}$ ) is also added to these polymer mixtures. Although the flexibility of maximizing both the charge transport and NLO activity separately in this class of PR polymers is restricted, this approach may have the advantage of allowing much larger concentrations of NLO chromophore in the polymer by eliminating the need for a separate charge transport agent and also allowing a choice of host polymer for maximum solubility of the dual function dopant. In addition, the PR response times of previous (relatively low-mobility) polymers were shown to be charge generation limited rather

than mobility limited when  $C_{60}$  is used as a sensitizer. Therefore the charge-transporting properties of a suitably chosen DFD may not be a limitation on the PR properties (particularly speed) of the polymer until the quantum efficiencies of charge generation of PR polymers are substantially improved. The DFD-based PR polymer system PMMA:DTNBI: $C_{60}$  exhibits two important properties not observed previously in PR polymers. The first is nondestructive reading in which the diffraction efficiency of the PR grating shows no decay under readout at sufficiently low intensity after 24 hours. The second property is optical trap activation, in which both the



diffraction efficiency and storage lifetime of the material are observed to increase substantially when the material is irradiated prior to writing the PR grating.

Figure 7 compares the photorefractive polymers developed under this ARPA supported contract with several inorganic PR crystals. For PR polymers, the maximum index change has improved by two orders of magnitude, implying a four order of magnitude change in diffraction efficiency (see Eq. (1)) and the speed has improved by four orders of magnitude from the first identified PR polymer bisA-NPDA:DEH. The PR sensitivity (indicated by the diagonal dotted lines in the Figure) is at this point equivalent to many of the best inorganic crystals.

#### IV. Understanding of Photorefractive Polymers

The polymer system PVK:FDEANST:TNF and systems like it show improvements in performance that cannot be explained by models based on the simple electrooptic PR effect that have worked so well for previously known PR polymers and crystals, even if it is assumed that the space-charge field actually approaches the externally applied field in value. In some PR polymer systems we have shown that a new orientational enhancement mechanism, unique to PR polymers, can result in substantial improvements in PR polymer performance.

In the standard model of the PR effect, the modulation in the index of refraction due to the internal space charge field is given by the electrooptic effect as indicated in Eq.(1). Since the electrooptic coefficient is generally assumed to be a constant in this model, it is useful to call this the "simple EO" model for the PR effect. The new orientational enhancement mechanism occurs in polymers in which the NLO chromophores are small molecule guests in the polymer matrix. The enhancement relies on the ability of the NLO chromophores to be aligned, not only by the externally applied electric field, but also *in situ* by the sinusoidally varying space-charge field during grating formation. The resulting spatially periodic poling of the sample leads to a modulation of the birefringence of the material and to a modulation of the electrooptic response, the combination of which contributes favorably to the diffracted fields in the proper polarization.

Figure 8 illustrates the effect schematically. The interfering light beams are assumed to produce a sinusoidally varying space charge field by the usual mechanisms of drift and diffusion. The externally applied electric field  $E_o$  will add to this field to produce a total field  $E_T$ . Since the nonlinear optical chromophores have orientational mobility due to the low  $T_g$  or to their relatively small molecular size, a spatially periodic orientational pattern is produced as the electric field orients the molecules by virtue of their ground state dipole moment. In the two center panels of

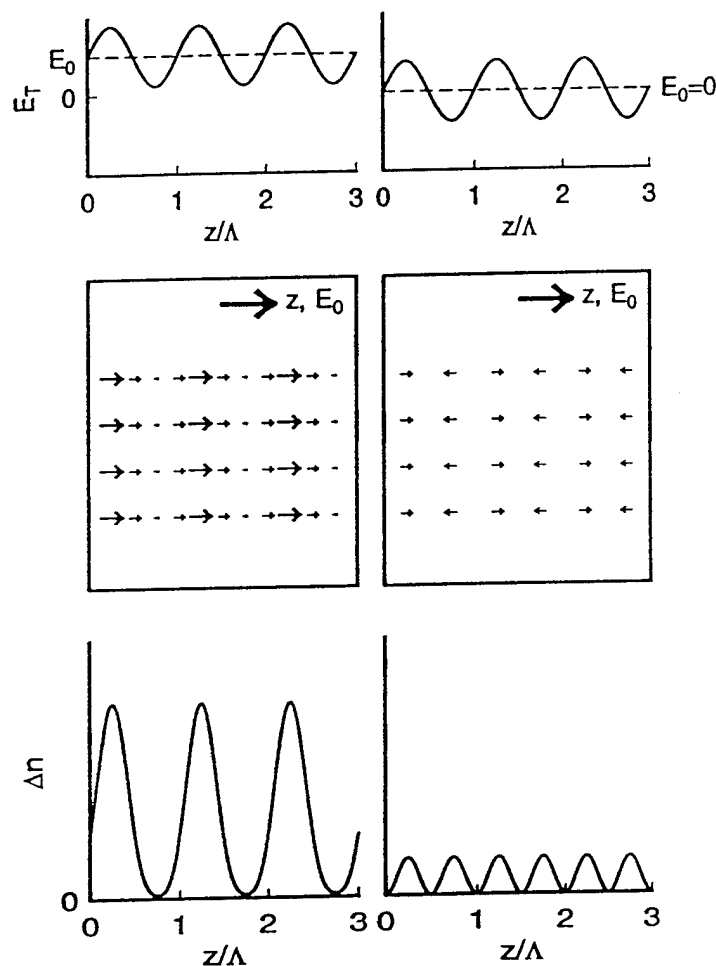


Figure 8. Schematic illustration of the periodic poling responsible for the orientational enhancement effect. For simplicity, the background bias field  $E_0$  and the space charge field are both directed along  $z$  in this figure, which would occur if the writing beams entered the sample from either side symmetrically. The magnitude of the total field is shown at the top for  $E_0 \neq 0$  (left) and  $E_0 = 0$  (right). The resulting average alignment of the chromophores is shown in the center and the resulting refractive index grating in the bottom panels.

the Figure, this effect is illustrated with arrows representing a locally averaged value of the molecular ground state dipole moment. The two writing beams are assumed to enter the sample

for the right and left sides of the Figure. If  $E_{sc}$  and  $E_o$  lie in the same direction, as shown, only the magnitude of the average local dipole moment will be periodic. In the more general case, where there is a component of  $E_o$  orthogonal to  $E_{sc}$ , the directions of the average local dipole moment will be periodic as well.

The effect of the periodic orientation is to produce a spatially modulated birefringence and a spatially modulated electrooptic coefficient, both of which can contribute to the scattered light field. For these two effects, the nonlinear response of the material is quadratic in the total local electric field; hence the orientational enhancement effect may be regarded formally as a  $\chi^{(3)}$  process. However, this orientational  $\chi^{(3)}$  arises from different physical processes than other  $\chi^{(3)}$  mechanisms previously reported. As the Figure illustrates (right side), if no dc electric bias field is present, the resulting modulation of the index of refraction is at twice the grating wavevector  $K_G$  of the intensity pattern. When a bias field is present (left side), the modulation appears at  $K_G$  as well and can contribute strongly to the first order Bragg diffracted beam. The orientational enhancement effect will be operative for any photorefractive polymer in which the nonlinear chromophores have the ability to reorient appreciably in response to the local electric field; in contrast, it will not be important for permanently poled photorefractive polymeric systems nor for photorefractive crystals, either inorganic or organic.

The discovery of the orientation enhancement mechanism was motivated by the observation that, for the measured diffraction efficiency and electrooptic coefficient, the calculated space charge field amplitude greatly exceeded the external applied electric field in PVK:FDEANST:TNF, a situation which simply cannot occur physically. The theory that we have developed leads to three predictions: (1) an enhanced diffraction efficiency arising from the

combined influence of both the modulated birefringence and electrooptic coefficients, (2) a change in the polarization anisotropy, and (3) presence of gratings with wavevectors of  $2K_g$ ,  $3K_g$ , etc., even with a purely sinusoidal space charge field. We have verified all three predictions experimentally for the case of PVK:FDEANST:TNF.

In trying to improve the sensitivity of polymer PR materials it is critically important to identify the limitations of the current classes of PR polymers. One possible limitation that is often mentioned is the relatively slow speed of response, especially relative to some of the semiconductor materials. The speed of formation of a space charge grating is proportional to the photoconductivity which in turn depends upon the quantum yield of photogeneration  $\phi$ , the carrier lifetime and the mobility  $\mu$  of the carriers. To increase the photoconductivity and hence the speed, it is often assumed that a materials with high mobility is required. This section shows by analysis of the photogeneration process that mobility limitations only occur when the photocharge generation process itself is sufficiently efficient.

The temporal response of a PR polymer can be assessed by using a simple model of the maximum sensitivity. It can be shown that there is a maximum sensitivity of a PR material, where in this context sensitivity is defined as the PR response (usually index change) per unit energy required to produce this response. This can equivalently be recast into a limitation on speed given a required beam-coupling gain, i.e.  $\Gamma/t$ . This model assumes that the rate limiting step to the formation of the PR space-charge field at a given wavevector is charge generation; once a charge is generated, the mobility is assume sufficiently high and the trapping sufficiently efficient that the charge contributes immediately to the PR grating. More precisely, it is assume that the transport length is optimal, that is, equal to the grating wavelength  $\Lambda_G$ . Any decrease in the rate of grating

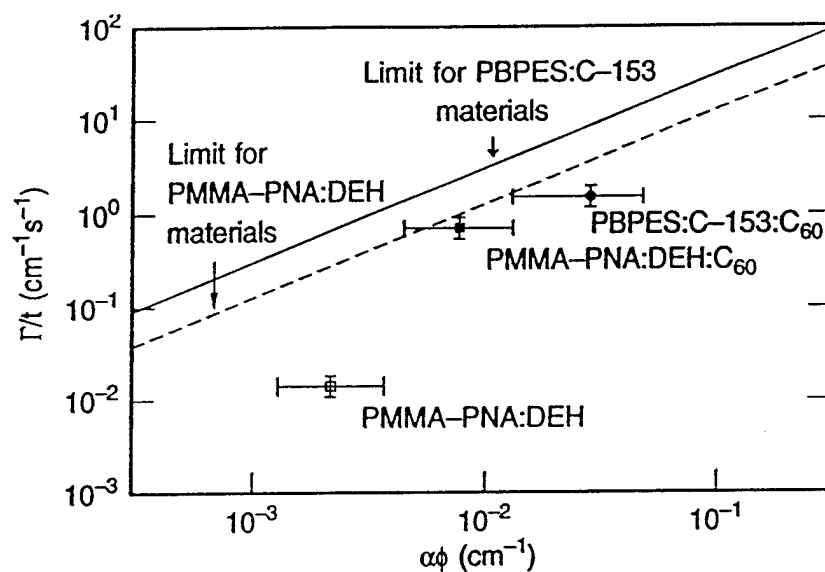


Figure 9. The maximum observed value of  $\Gamma/t$  shown as a function of  $\alpha\phi$  for PMMA-PNA:DEH (open square), PMMA-PNA:DEH:C $_{60}$  (filled square), and PBPEs:C-153:C $_{60}$  (circle). Also shown are the theoretical limits based on the charge generation limited model for the PMMA-PNA:DEH materials (dashed line) and PBPEs:C-153:C $_{60}$  (solid line).

formation due to inefficient transport and trapping should cause the measured  $\Gamma/t$  to fall below the value predicted by the model.

For the PR polymer PMMA-PNA:DEH, both with and without sensitizing agent, experimental measurements fix a linear relationship between  $\Gamma/t$  and  $\alpha\phi$ , indicated by the dashed line in Figure 9. For the actual material (with no explicit sensitizer), the value observed for  $\Gamma/t$  falls well below the fundamental limit for the measured values of  $\alpha$  and  $\phi$  (open square in the Figure). For the polymer doped with 0.1wt% C $_{60}$ , the maximum value of  $\Gamma/t$  increases to a value near the predicted limit for the measured values of  $\alpha$  and  $\phi$  (filled square). This is due to both an



increase in the value of  $\Gamma$  and a decrease in the response time  $t$ . It has been suggested previously that the addition of  $C_{60}$  increases the concentration of traps in this PR polymer. Since the addition of 0.1wt% of  $C_{60}$  should have negligible effect on the mobility, it is most likely the improvement in trapping that raises the performance of this materials to the generation limit. Without increasing the value of  $\phi\alpha$ , further increases in the mobility or more efficient charge transport should not improve the gain growth rate by a substantial amount in this polymer.

The poly(silane)-based polymer PBPEs:C-153: $C_{60}$  provides an example to illustrate the charge generation limit for a sample with much higher mobility (and different  $\phi\alpha$ ). In this material, the mobility at high fields is approximately 2 to 3 orders of magnitude higher than in other PR polymers. The generation limit for this system is indicated by the solid line in Figure 9. The peak value for  $\Gamma/t$  is shown in the Figure by the filled circle. The experimentally determined value of  $\Gamma/t$  falls further below the line for the PBPEs:C-125: $C_{60}$  sample than for the PMMA-PNA:DEH: $C_{60}$  sample. A slightly higher value of  $\Gamma/t$  is achieved in the poly(silane)-based material due to a combination of increases in the product of  $\alpha\phi$ , the mobility, and possibly improved trapping. Since  $\alpha\phi$  increases by a factor of 3 and  $\mu$  increases by a factor of 100, the modest sized of the increase in  $\Gamma/t$  implies relatively inefficient trapping dynamics compared to PMMA-PNA:DEH: $C_{60}$ .

From the results summarized in Figure 9, it is clear that the PR performance of these materials is not mobility limited. An increase in  $\mu$  by 2 orders of magnitude has only a small effect on the measured  $\Gamma/t$ . Optimization of the traps should lead to faster performance much closer to the generation limit. Since the total absorption of the material will likely be bounded by thermal

and photochemical effects which can occur at large  $\alpha$ , the route to even faster organic PR polymers lies in increasing the quantum efficiency of charge generation either through higher applied fields or intrinsically more efficient sensitizers.

## V. Optimization of Performance for Power Limiting Applications

The important parameters for power limiting are found to be the experimental decay times of the beams transmitted through the photorefractive materials and the steady state transmission at very long times. An important photorefractive materials constant  $A$  has been defined with units of energy density.  $A$  decreases in value with increasing holographic diffraction figure of merit  $Q$  and determines the energy density where limiting occurs.  $Q$  is defined by the equation

$$Q = n^3 r_e / \epsilon \quad (2)$$

Here  $n$  is the index of refraction and  $\epsilon$  the dielectric constant.

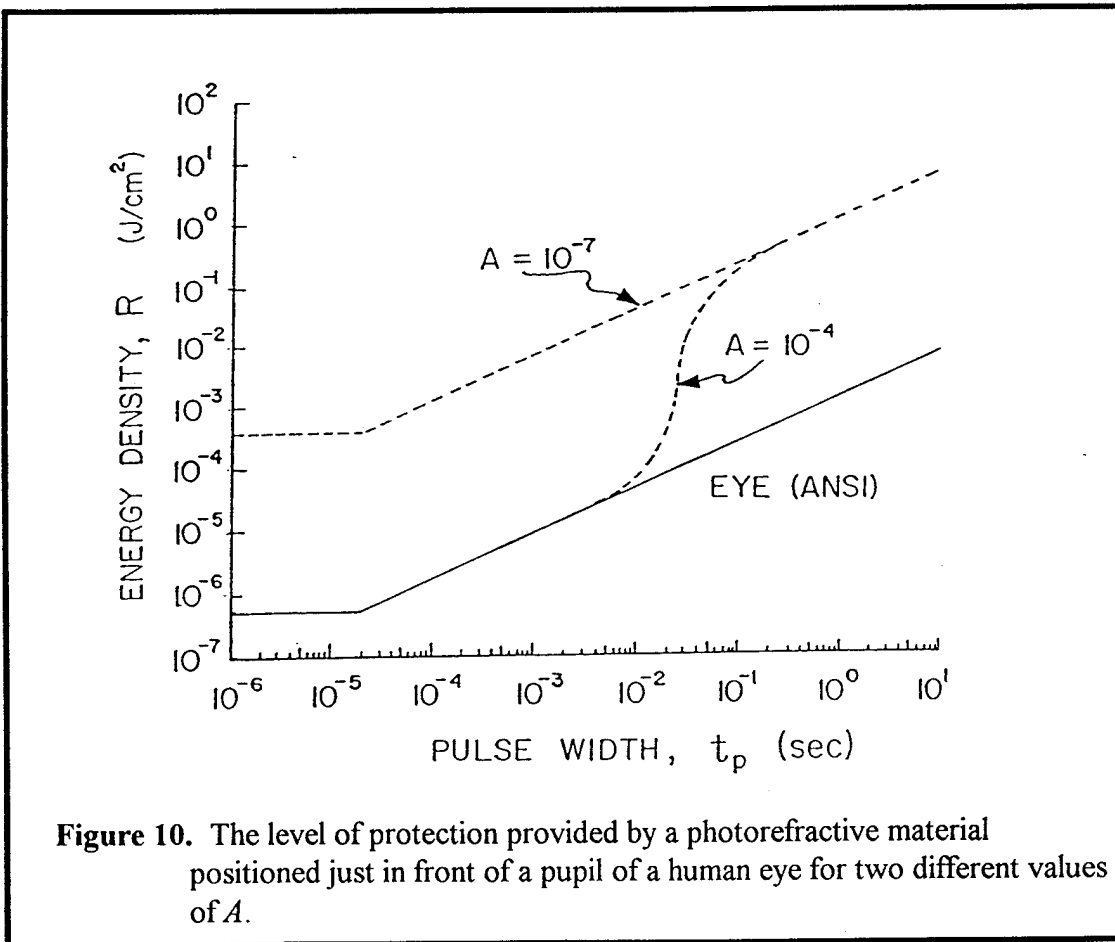
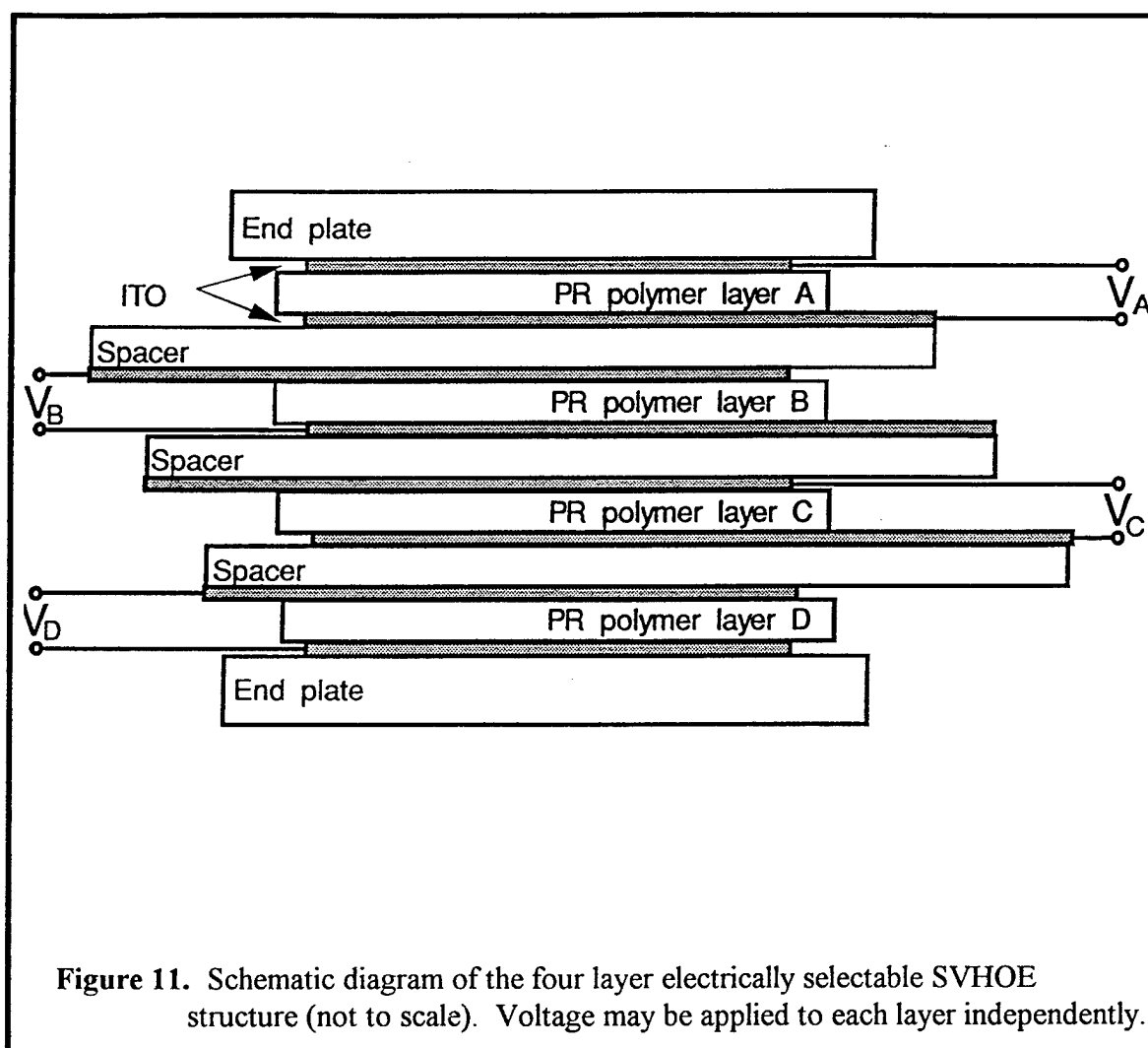


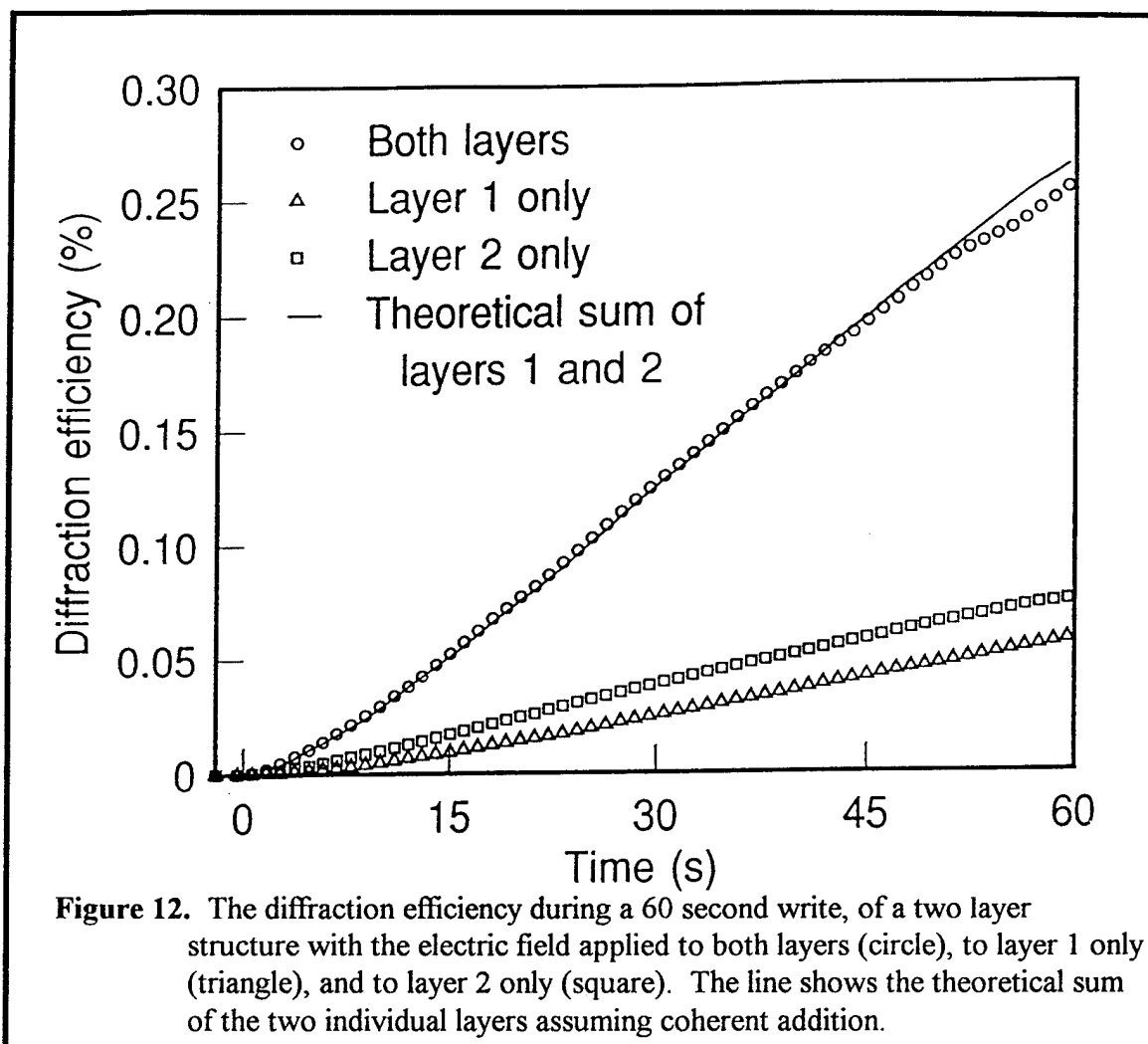
Figure 10 shows the level of protection provided by a photorefractive material positioned in front of a human eye pupil for two different values of  $A$ . It can be seen that materials with  $A$  values of  $10^{-7}$  J/cm<sup>2</sup> or less provide significant protection for pulse widths as short as  $10^{-6}$  s while materials with  $A$  values on the order of  $10^{-4}$  J/cm<sup>2</sup> provide protection only for pulse widths of  $10^{-1}$  s or longer. Known inorganic photorefractive materials such as BaTiO<sub>3</sub> have  $A$  values of approximately 1 J/cm<sup>2</sup>, so clearly it is necessary to develop photorefractive materials with much higher diffraction figures of merit  $Q$  in order to provide direct protection of the human eye by photorefractive beam fanning. According to Figure 7, the performance of the PR polymers identified to date is equal to and in some cases better than that for the inorganic crystals. The current class of PR polymers, however, still do not have the three to four orders of magnitude improvement in  $Q$  that would make them immediately useful in power limiting applications. On the other hand, as the previous section has shown, improvements in photocarrier generation quantum yield, could in principal yield this improvement in performance.

Although some of the intrinsic properties of PR polymers are comparable with those of inorganic PR crystals, one of the major limitations in achieving useful device performance in these materials (such as high diffraction efficiency and the observation of beam fanning) has been the relative thinness of the samples (<350 $\mu$ m) fabricated to date. Increasing the thickness of the monolithic PR polymer samples in the conventional geometries investigated is not practical, because large applied electric fields are necessary for the observation of PR effects in these materials. Producing large electric fields across thick samples would require extremely large potentials (of the order of  $4 \times 10^5$  V for a 1 cm. thick sample). In addition, the maximum field that can be applied across a polymer film has been observed to decrease substantially with



increasing film thickness. One solution to this problem is to extend the concept of stratified volume holographic optical element (SVHOE) structures to PR polymers, in which layers of PR polymers are interspersed with buffer layers containing transparent electrodes that allow fields to be applied across the individual layers.

We have fabricated and made measurements on holographic gratings written in SVHOE structures of consisting of multiple thick ( $>100\mu\text{m}$ ) layers of the PR polymer PMMA:DTNBI:C<sub>60</sub>, in which each layer operates in the Bragg diffraction regime. Figure 11 shows the SVHOE structure schematically. Coherent addition of diffracted fields from the individual layers is



observed, leading to a diffraction efficiency that increases with the square of the active layer thickness. This phenomenon is shown in Figure 12.

## VI. RECOMMENDATIONS FOR FUTURE RESEARCH

As discussed in the previous Section, two things currently limit photorefractive polymers in eye and sensor protection applications - the speed of the photorefractive response and the thinness of the samples. Future research should concentrate in these two areas.

We have shown that the response speed is currently limited by the quantum yield for the generation of mobile charge carriers in the polymer systems. This quantum yield is a very sensitive function of the applied external electric field. Because of the low dielectric constant of polymer systems when compared to inorganic systems, the initially generated electron/hole pair can recombine more easily in a process called geminate recombination. In order to overcome this efficient recombination process, an external electric field must be applied to keep the charges separated. To improve the charge carrier generation quantum yield, one can either develop methods for reducing the efficiency of the geminate recombination process or develop material preparation techniques that increase the maximum electric field that can be applied across the thin film samples.

The second area for future work involves developing techniques for producing thick ( $>500\mu\text{m}$ ) samples in which beam fanning can be observed. Here the problem is to produce thick samples that can simultaneously be electric field poled to orient the chromophores and, as discussed in the last paragraph, to enhance the charge carrier generation quantum yield. In the previous section, we have described a stratified volume approach to this problem. The production of multiple layers of photorefractive polymer films with thin buffer layer spacers is an arduous task. Work needs to continue on improving this approach as well as searching for other techniques to produce thick photorefractive polymer films.

## APPENDIX - Publications

1. S.M. Silence, C.A. Walsh, J.C. Scott, T.J. Matray, R.J. Twieg, F. Hache, G.C. Bjorklund, W.E. Moerner, "Subsecond grating growth in a photorefractive polymer", *Opt. Lett.* **17**, 1107 (1992).
2. C.A. Walsh, W.E. Moerner, "Two beam coupling measurements of grating phase in a photorefractive polymer", *J. Opt. Soc. Am. B, Opt. Phys.* **9**, 1642 (1992).
3. J.C. Scott, L.T. Pautmeier, W.E. Moerner, "Photoconductivity studies of photorefractive polymers", *J. Opt. Soc. Am. B, Opt. Phys.* **9**, 2059 (1992).
4. S.M. silence, C.A. Walsh, J.C. Scott, W.E. Moerner, " $C_{60}$  sensitization of a photorefractive polymer", *Appl. Phys. Lett.* **61**, 2967 (1992).
5. J.C. Scott, L. Th. Pautmeier, WE. Moerner, "Photoconduction and photorefraction in molecularly doped polymers", *Synth. Met.* **54**, 9 (1992).
6. M.C.J.M. Donckers, S.M. Silence, C.A. Walsh, F. Hache, D.M. Burland, W.E. Moerner, R.J. Twieg, Net two beam coupling gain in a polymeric photorefractive material", *Opt. Lett.* **18**, 1044 (1993).
7. S.M. Silence, J.C. Scott, F. Hache, E.J. Ginsburg, P.K. Jenkner, R.D. Miller, R.J. Twieg, W.E. Moerner, "Poly(silane) based high mobility photorefractive polymers", *J. Opt. Soc. Am. B, Opt. Phys.* **10**, 2306 (1993).
8. S.M. Silence, F. Hache, M. Donckers, C.A. Walsh, D.M. Burland, G.C. Bjorklund, R.J. Twieg, W.E. Moerner, "Nonlinear optical properties of photorefractive polymers", *Proc. SPIE* **1852**, 253 (1993).
9. S.M. Silence, M.C.J.M. Donckers, C.A. Walsh, D.M. Burland, W.E. Moerner, R.J. Twieg, "Electric field dependent nonphotorefractive gratings in a nonlinear photoconducting polymer", *Appl. Phys. Lett.* **64**, 712 (1994).
10. W.E. Moerner S.M. Silence, F. Hache, G.C. Bjorklund, "Orientationally enhanced photorefractive effect in polymers", *J. Opt. Soc. Am. B, Opt. Phys.* **11**, 320 (1994).
11. S.M. Silence, M.C.J.M. Donckers, C.A. Walsh, D.M. Burland, R.J. Twieg, W.E. Moerner, "Optical properties of poly(N-vinylcarbazole) based guest host photorefractive polymer systems", *Appl. Opt.* **33**, 2218 (1994).
12. J.J. Stankus, S.M. Silence, W.E. Moerner, G.C. Bjorklund, "Electric field switchable stratified volume holograms in photorefractive polymers", *Opt. Lett.* **19**, 1480 (1994).
13. S.M. Silence, R.J. Twieg, G.C. Bjorklund, W.E. Moerner, "Quasinondestructive readout in a photorefractive polymer", *Phys. Rev. Lett.* **73**, 2047 (1994).
14. S.M. Silence, G.C. Bjorklund, W.E. Moerner, "Optical trap activation in a photorefractive polymer", *Opt. Lett.* **19**, 1822 (1994).



15. J.J. Stankus, S.M. Silence, R.J. Twieg, D.M. Burland, R.D. Miller, J.C. Scott, W.E. Moerner, G.C. Bjorklund, "Recent progress in photorefractive polymers: materials and structures", *Proc. SPIE* **2285**, 204 (1994).
16. W.E. Moerner, S.M. Silence, "Polymeric Photorefractive Materials", *Chem. Rev.* **94**, 127 (1994).
17. S.M. Silence, J.C. Scott, J.J. Stankus, W.E. Moerner, C.R. Moylan, G.C. Bjorklund, R.J. Twieg, "Photorefractive Polymers Based On Dual-Function Dopants", *J. Phys. Chem.* **99**, 4096 (1995).
18. D.M. Burland, G.C. Bjorklund, W.E. Moerner, S.M. Silence and J.J. Stankus, "Photorefractive Polymers - A Status Report", *Pure and Appl. Chem.* **67**, 33 (1995).
19. S.M. Silence, D.M. Burland, W.E. Moerner, "Photorefractive Polymers", in **The Photorefractive Effect**, D.D. Nolte, ed., Electronics Materials: Science and Technology Series (Kluwer Academic Press, Boston, 1995).
20. C. Poga, D.M. Burland, T. Hanemann, Y. Jia, C.R. Moylan, J.J. Stankus, R.J. Twieg and W.E. Moerner, "Photorefractivity in new organic polymeric materials", in press (1995).